

2p

Comp. Auth.  
 NASA. Lewis  
 Research Center  
 Cleveland, Ohio

N64-17562<sup>pw</sup>  
 Code None

William A. Dugraw et al  
 Repr. from Anal. Chem.  
 v. 36, Feb. 1964 0430-43, refs

(NASA RP-142)

## Determination of Oxygen in Potassium

SIR: Much interest has been evidenced recently in the use of potassium as a thermodynamic working fluid in nuclear turboelectric power systems. Since oxygen impurities in alkali metals (even below 20 p.p.m. in some cases) have been recognized as promoting and accelerating corrosion attack on containment materials, it is important that a reliable method for determining the oxygen content of potassium be available.

Currently the technique most widely used for the measurement of oxygen in potassium is the Pepkowitz-Judd amalgamation technique (2). It is our belief that a major source of error in this technique is the inadvertent introduction of oxygen or water contamination during the processes of sampling, transfer, and analysis. This should not be unexpected in view of the reactivity of potassium with oxygen and water and the questionable handling techniques currently employed. It then follows, if the above contention is correct, that extreme care must be exercised in the handling and analytical procedures. One way to prevent oxygen pickup is to carry out all steps in a high vacuum environment with a continuous monitoring of the pressure by means of a high vacuum gauge.

In our attempt to improve the analytical precision of the Pepkowitz-

Judd technique for determining oxygen in potassium, five innovations were made: the entire system complex—sample tube, transfer section, and amalgamation system—was maintained under a high vacuum; the amalgamation reaction system volume was made small; a ball check valve was used to contain the vigorous amalgamation reaction; flanged O-ring joints were used to eliminate greased or waxed joints; and replicate samples were taken from a single sample tube.

The apparatus, shown in Figure 1, consists of two major components: a metal extruder and a glass extraction system. The glass and metal components are connected by O-ring joints, and the entire apparatus is evacuated to a pressure between  $2 \times 10^{-5}$  and  $4 \times 10^{-6}$  torr.

The sample container is a stainless-steel tube  $6\frac{3}{4}$  inches by  $\frac{5}{16}$ -inch i.d.

It is vacuum filled with liquid metal, capped, and stored under vacuum until used. For analyses, the sample tube is mounted in the extruder section apparatus.

After the apparatus has attained operational vacuum, a small portion of the potassium is extruded from the sample tube, cut with a hot wire, and discarded in the waste tray. The analytical sample is then extruded, cut off, and dropped into the glass extraction system. The extruder is valved-off from the extraction system and the ball check valve is seated in place to confine the amalgamating reaction. Triple distilled mercury is then admitted to the extraction system. After the reaction has occurred, manipulation of a glass-covered magnetic bar within the extraction system removes all film from the chamber walls. By means of a valve on the restricted end of the extraction system, the amalgam is slowly removed into the receiving flask. The exit valve is

Table I. Oxygen Content of Potassium

Lot	Tube number	Oxygen, p.p.m.	Sample weight, grams
A	1	13, 18, 18	1.06, 1.22, 1.13
	2	23, 21, 22	0.61, 1.40, 2.06
B	3	88, 96, 88	1.15, 1.14, 1.16
C	4	88, 93, 93	0.66, 0.88, 1.22
D	5	186, 198	0.74, 1.00
E	6	207, 200, 196	1.07, 1.03, 1.06

Reprint/

Table II. Relation of Oxygen Pickup to Time

Lot	Tube number	Oxygen, p.p.m.	Sample weight, grams
B	7	88 <sup>a</sup>	0.66
		93, 98 <sup>b</sup>	0.66, 1.29
		89 <sup>c</sup>	0.79

<sup>a</sup> Procedure as in Table I.

<sup>b</sup> Triple distilled mercury, 24 hours hold.

<sup>c</sup> Oxifier reclaimed mercury, 24 hours hold.

closed, and approximately 15 ml. of mercury is admitted to the extraction system and the magnetic bar manipulation is repeated. The wash mercury is removed as before. A total of five similar washes is made to remove completely the potassium amalgam; approximately 700 to 900 grams of mercury are used in all.

The glass extraction portion of the system is brought to atmospheric pressure and the extraction system and amalgam receiving flask are removed. Up to this point, the total time for the operation is approximately 1 hour.

The potassium is extracted from the amalgam using boiled distilled water and titrated with standard sulfuric acid to determine the weight of alkali sample used.

The potassium oxide is washed out of the extraction chamber using boiled distilled water and titrated with standard 0.005*N* sulfuric acid using a microburet. Methyl red is used as an indicator in both titrations.

The following values for oxygen content, Table I, clearly indicate a good degree of reproducibility. Each set of analytical values represents replicate potassium samples extruded from the same sample tube.

To establish whether the amalgam

Table III. Relation of Oxygen Pickup to Pressure

Lot	Tube number	Oxygen, p.p.m.	Sample weight, g	Pressure, torr
B <sup>a</sup>	8	194, 209	0.59, 0.60	$2 \times 10^{-3}$
		127, 117	0.74, 0.77	$4 \times 10^{-4}$

<sup>a</sup> Same lot as in Tables I and II, 90 p.p.m. oxygen.

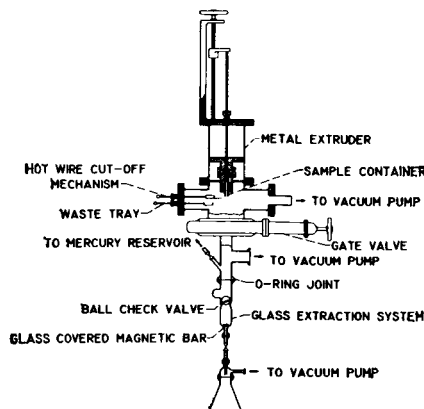


Figure 1. Alkali metal analytical apparatus

would react with the glass extraction system as a function of time, resulting in oxygen "pick-up," three tests were performed. The alkali metal was extruded and amalgamated as usual. Then prior to extraction, the amalgam was retained in the extraction system for 24 hours. The oxygen values obtained, as shown in Table II, indicated no dependence on residence time in the extraction system, up to 24 hours (the longest time studied).

If our contention is correct, that a high vacuum analytical system is necessary for reproducible results, it follows that a poor vacuum would be a

source of positive error. Tests performed at  $2 \times 10^{-3}$  and  $4 \times 10^{-4}$  torr confirm this. The oxygen values obtained are given in Table III.

It has been long recognized that it is difficult to ascertain the accuracy of the amalgamation technique because of technical problems associated with adding known increments of oxygen to potassium metal. This problem still has not been overcome; however, the analytical results presented here demonstrate that good precision can be obtained if the amalgamation technique is used at a pressure between  $2 \times 10^{-5}$  to  $4 \times 10^{-6}$  torr.

After completion of our partial investigation, we received a translation of a Russian report (1) describing their amalgamation technique in a vacuum environment.

#### LITERATURE CITED

- (1) Malikova, Y. D., Turovtseva, Z. M., *Analiz Gazov V Metalakh Akad. Nauk SSSR (English Transl.)* **FTD-TT-62-1338**, 1962.
- (2) Pepkowitz, L. P., Judd, W. C., *ANAL. CHEM.* **22**, 1283 (1950).

WILLIAM A. DUPRAW  
JUDSON W. GRAAB  
RANDALL F. GAHN

Lewis Research Center  
National Aeronautics and Space  
Administration  
Cleveland, Ohio

CASE FILE COPY